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AB-INITIO MOLECULAR DYNAMICS SIMULATIONS OF MOLTEN Ni-BASED SUPERALLOYS (Preprint)

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14. ABSTRACT
In casting of single-crystal turbine blades for jet engines, the formation of solidification defects has become an increasingly important problem due to the rising levels of refractory elements in Ni-based superalloys. Refractory elements, which are beneficial for high-temperature mechanical properties, enhance density-driven convective instabilities underlying the formation of freckle defects in directional solidification. In support of an effort aimed at the development of validated mathematical criteria for predicting solidification-defect formation in superalloys, ab-initio molecular dynamics simulations have been performed to calculate volumes of Ni-AI, Ni-W, Ni-Re, Ni-Ta, Ni-Al-Re, Ni-Al-Ta, Ni-Al-W, and complex chemistries approximating RENE-N4 melts.

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Ab-Initio Molecular Dynamics Simulations of Molten Ni-Based Superalloys

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Introduction : In casting of single-crystal turbine blades for jet engines, the formation of solidification defects has become an increasingly important problem due to the rising levels of refractory elements in Ni-based superalloys. Refractory elements, which are beneficial for high-temperature mechanical properties, enhance density-driven convective instabilities underlying the formation of freckle defects in directional solidification. In support of an effort aimed at the development of validated mathematical criteria for predicting solidification-defect formation in superalloys, *ab-initio* molecular dynamics simulations have been performed to calculate volumes of Ni-Al, Ni-W, Ni-Re, Ni-Ta, Ni-Al-Re, Ni-Al-Ta, Ni-Al-W and complex chemistries approximating RENE-N4 melts.

Objective : Derive physical quantities related to the formation of highly mis-oriented grains during the solidification of single-crystal Ni-based superalloys. During directional solidification, the mass-density difference between the hot liquid near the solid-liquid interface and the cooler melt at the top and side-walls of the casting, is the driving force for convection and associated formation of solidification defects. This mass-density difference originates from both the composition and temperature dependencies of the liquid-phase molar volume ($V(c,T)$).

Methodology : The properties of molten Ni-based alloys are computed within the framework of *ab-initio* molecular dynamics (AIMD) simulations. For 500-atom simulations, ionic positions were evolved in time employing classical molecular dynamics in a constant-temperature and volume ensemble, using interatomic forces computed directly within the framework of electronic density functional theory (DFT). This implementation of AIMD made use of the commercial DFT software VASP (Vienna ab-initio simulation package). Nearly linear scaling is achieved for 500-atom calculations run on up to approximately 128 processors on an SGI O3K and Altix. In the last year the AIMD method was extended to treat constant temperature and pressure simulations, significantly reducing the computational effort required to derive the liquid metal densities.

Results : Simulations were performed for elemental, binary and ternary alloys of Ni with Al, W, Ta and Re to compute equations of state at temperatures of 1830 and 1750 K. Where comparisons with measurements are available, AIMD-calculated volumes agree to within 0.6–1.8% of experiment. The results also show the limitations of experimentally based parameterizations of the molar volumes for multicomponent liquid alloys, which for some systems give rise to qualitatively incorrect predictions for alloys with high concentrations of transition metal elements (e.g. W). Currently we are running calculations of the Ni-based superalloy RENE-N4 to obtain the liquid molar volumes realized during the directional solidification of these alloys. The AIMD results establish the limits of the accuracy of current density models used in commercial casting software and offers a new path for systematically improving them.

Significance to DoD : All weapons systems that employ Ni-based super-alloys in propulsion, energy generation, thermal protection systems or other high temperature applications will benefit from this research. Relevant systems include: current and future turbine powered aircraft, hypersonic vehicles and space lift/re-entry systems. The problem of freckle formation is particularly relevant to improving the properties of turbine-blades and thus the performance (efficiency and thrust–weight ratio) of high performance jet engines.

ab-Initio Molecular Dynamics Simulations of Molten Ni-Based Superalloys

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In the casting of single-crystal turbine blades, the composition (c) and temperature (T) dependencies of the liquid-phase molar volume ($V(c,T)$) play a critical role in driving convective instabilities and the associated formation of solidification defects. In support of a current effort aimed at the development of validated mathematical criteria for predicting the formation of solidification defects in Ni-based superalloys, *ab-initio* molecular dynamics (AIMD) simulations have been performed for elemental, binary and ternary alloys of Ni with Al, W, Re, and Ta, as well as a RENE-N4 multi-component superalloy, to compute equations of state at temperatures of 1830 and 1750 K. Where comparisons with measurements are available, AIMD-calculated volumes agree to within 0.6–1.8% of experiment. The results are used to test the accuracy of the predictions of the most recently published parameterization for composition and temperature dependent molar volumes in liquid multicomponent superalloys. Structural analysis based on radial distribution functions augmented with common-neighbor analysis and bond angle distributions reveal a strong tendency for icosahedral short range order for Ni-W and Ni-Re alloys. Also a new constant pressure methodology was added to the AIMD package that has allowed the efficient simulation of highly complex alloys such as an eight component model of a Rene-N4 Ni-based superalloy.

I. INTRODUCTION

In the casting of single-crystal turbine blades for high-performance jet engines, the formation of solidification defects has become an increasingly important problem due to the rising levels of refractory elements in commercial Ni-based superalloys. While refractory elements have the desirable effect of improving high-temperature creep strength, they also enhance density-driven convective instabilities underlying the formation of so-called freckle defects (chains of small equiaxed grains) in directional solidification. The high-angle grain boundaries and composition gradients associated with freckles adversely effect mechanical properties of these components. The optimization of superalloys for high-performance applications requires a quantitative model for predicting refractory metal compositions which will allow commercial castings that avoid these defects. Freckles develop due to thermo-solutal convection in the molten alloy during solidification, and it has been suggested that they will form when a critical Rayleigh number is exceeded.[1–4] The Rayleigh number (R) is a measure of the ratio of the buoyancy force to the retarding frictional force in the mushy zone:

$$R = (\Delta\rho/\bar{\rho})gKl/\alpha\nu \tag{1}$$

where l is an appropriate length scale, K is the average permeability, g gravitational acceleration, α is the thermal diffusivity, ν is the kinematic viscosity of the fluid, and $(\Delta\rho/\bar{\rho})$, the density contrast, is a measure of the density variation over the mushy zone between the solid and liquid phases. The tendency towards defect formation is highly sensitive to the primary dendrite arm spacing (which determines the permeability), as well as the density contrast. An open question concerning the predictive power of the Rayleigh-number criterion for freckle formation is the fact that it assumes the density gradients are aligned with gravity. This is not the case in most castings since heat losses through the mold create horizontal thermal gradients and hence tilted solid-liquid interfaces. The work presented in this paper is a component of a multi-institutional effort, supported through the Air Force Office of Scientific Research Materials Engineering for Affordable New Systems (AFOSR-MEANS) program, aimed at the development of validated mathematical criteria for predicting solidification-defect formation in the casting of single-crystal Ni-based superalloys. A multicomponent RENE-N4 superalloy has been chosen as the focus of experimental and modeling efforts aimed at validating these criteria.

To validate mathematical models for freckle formation in specific alloy systems, it is critical that the values of the various parameters in Eq. 1 are accurately known. Determination of the permeability and density gradients poses a major challenge in this regard. In the MEANS project, values for the permeability are being derived from fluid-flow simulations employing realistic models for the mushy-zone topology obtained from three-dimensional reconstructions derived by serial sectioning.[5] The focus of the work presented here, performed with HPC Challenge support, is the application of *ab-initio* molecular dynamics (AIMD) simulations as a computational framework for aiding the development and validation of accurate models for $\Delta\rho$. In directional solidification, $\Delta\rho$ represents the mass-density difference between the hot liquid near the dendritic solid-liquid interface and the cooler melt at the top and side-walls of the casting. The density contrast is therefore related both to the temperature gradients present during casting, as well as the variations in solute concentration in the melt that develop as a consequence of equilibrium partitioning

between solid and liquid phases. The mass-density difference thus originates from both the composition (c) and temperature (T) dependencies of the liquid-phase molar volume $V(c,T)$.

Recently, Mukai *et al.*[6–8] performed extensive measurements of the densities of several binary liquid Ni-based alloys, and a few representative ternaries, as functions of c and T. The results of their measurements have been used to develop a thorough parameterization for $V(c,T)$ in superalloys.[8] Due to the lack of sufficient data for multicomponent systems, a key assumption made in the development of the parameterization is that the partial-molar volume of each solute is independent of the compositions of the other species. The effects upon $V(c,T)$ arising from the interactions between solute atoms of different types are thus neglected. Further, measured density data for some key elements such as Re are unavailable and the parameters for these elements are treated as parameters to fit available data for multicomponent superalloys. Comparisons between the predictions of the Mukai parameterization and available data for densities of commercial superalloys shows agreement at the level of a few percent. We are unaware of experimental data for the composition and temperature dependent densities in the multicomponent RENE-N4 superalloy, and estimates of the accuracy of the Mukai model for liquid density in this system, which forms the focus of current experimental efforts within our MEANS project, are thus not readily obtained. In the current work we are using of state-of-the-art AIMD simulations as a means for testing the accuracy of the model for parameterizing $\rho(c,T)$ in this system. These calculations are also being used to independently test the accuracy of the Mukai parameters for elements where direct measurements of liquid density are unavailable.

II. METHOD

The properties of molten Ni-based alloys have been computed within the framework of *ab-initio* molecular dynamics (AIMD) simulations. For simulations of elemental, binary and ternary alloy melts, ionic positions were evolved in time employing classical Nosé-Hoover dynamics [9, 10], appropriate for a fixed-number, volume and temperature (NVT) ensemble, using interatomic forces computed directly within the framework of electronic density functional theory (DFT). The current implementation of AIMD makes use of the commercial DFT software VASP (Vienna ab-initio simulation package),[11–13] developed at the Institut für Materialphysik of the Univerität Wien. The VASP code scales well for systems with large numbers of atoms on parallel computers with high-bandwidth communications networks. The computational problem involves repeated applications of fast-fourier-transform and iterative diagonalization algorithms. While the problem is far from embarrassingly parallel overall, nearly linear scaling is achieved for representative calculations up to approximately 128 processors for AIMD runs performed on an SGI O3K and Altix, as we have documented previously.[15] The underlying algorithms employed in VASP have been extensively tested and optimized for parallel processing with large numbers of processors. Most of the production runs reported here were performed on 64 processors.

In order to improve the efficiency of the calculations the current version of VASP (release 4.6.31) was modified to integrate the molecular dynamics equations appropriate for the NPT (fixed number, pressure and temperature) ensemble using the *ab-initio* computed forces and pressures. Following standard approaches we first derived the equations for Parrinello-Rahman dynamics using (deterministic) Nosé-Hoover chain thermostats for the atoms and the simulation cell vectors. Next we derived the equations for Parrinello-Rahman dynamics using Langevin thermostats with stochastic forces and pressure tensors. These two mathematically distinct algorithms for computing NPT trajectories were then used to perform crucial self-consistency checks. The dynamics are constrained to eliminate center-of-mass motion and to impose irrotational deformations on the simulation cell and a further option restricts deformations to volumetric (shape-preserving) fluctuations. Minimal changes were made to the VASP source code to include this new AIMD option and to accommodate the required input and output parameters.

Below we present NVT results obtained to date for twelve elemental, binary and ternary alloy compositions, which are referred to in terms of the number of each type of atom in the simulation cell: Al_{500}, Ni_{500}, $Ni_{400}Al_{100}$, $Ni_{473}W_{27}$, $Ni_{400}W_{100}$, $Ni_{473}Re_{27}$, $Ni_{400}Re_{100}$, $Ni_{473}Ta_{27}$, $Ni_{400}Ta_{100}$, $Ni_{436}Al_{50}W_{14}$, $Ni_{436}Al_{50}Re_{14}$ and $Ni_{436}Al_{50}Ta_{14}$. The details of the NVT calculations were described previously[15, 16] and are only briefly summarized here. Nosé-Hoover equations of motion were integrated specifying thermostat temperatures of T=1830 and T=1750 K. The time steps (Δt) for the MD simulations were chosen as Δt=0.002 ps or Δt=0.003 ps, to ensure that the conserved energy in the Nosé-Hoover dynamics displayed a drift in time no larger than 1 meV/atom·ps. The starting configuration for the Al_{500}, Ni_{500} and $Ni_{400}Al_{100}$ simulations were obtained from snapshots derived from classical molecular-dynamics simulations employing semi-empirical interatomic potentials [19]; for the Ni-W, Ni-Re, Ni-Ta, Ni-Al-W, Ni-Al-Re and Ni-Al-Ta simulations the initial configurations were obtained by replacing Ni and Al atoms, selected at random, by W, Re or Ta. At each MD time step the self-consistent charge density and associated interatomic forces were computed for integration of the ionic trajectories, and relevant system properties including the pressure, energy, temperature and atomic coordinates were stored. The DFT calculations made use of ultrasoft pseudopotentials [20, 21] and the PW91 generalized-gradient approximation (GGA).[22] The electronic wavefunctions were represented in a plane-wave basis set with a cutoff energy of 260 eV. The simulations employ a single k-point (Γ) in performing reciprocal-space summations, with electronic eigenvalues occupied according to Fermi statistics with an electronic temperature equal to that for the ions. For each alloy composition simulations were performed over a range of volumes spanning plus or minus five percent of the experimentally measured or estimated equilibrium value. Total simulation times ranged from 5–10 ps, a time interval long enough to obtain good statistical precision in calculated equation-of-state parameters.[15]

For the RENE-N4 calculations target temperatures and chemistries were calculated using PANDAT by Cumputherm

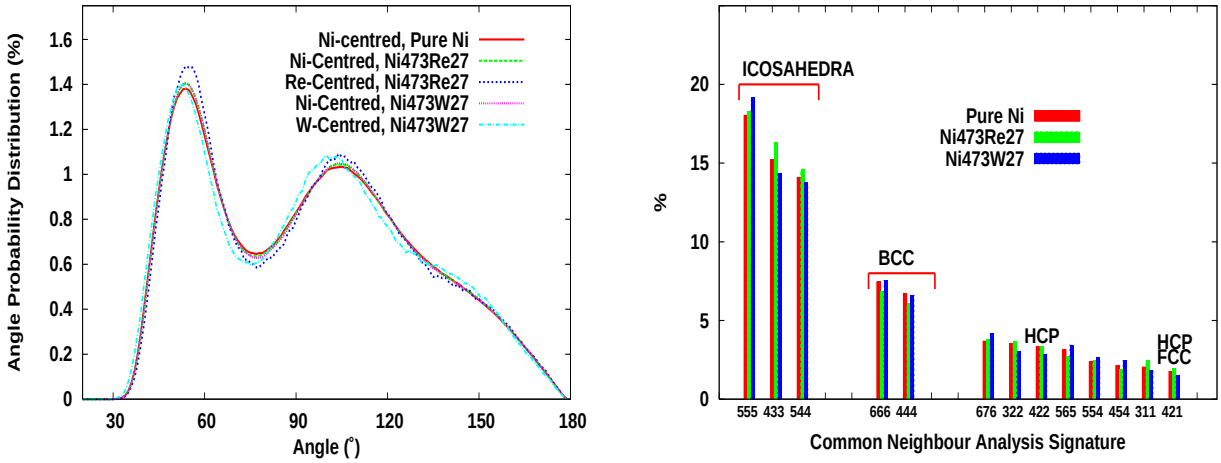

FIG. 1: Angle probability distribution function (left) and Common Neighbor Analysis (right) for pure Ni, $Ni_{473}Re_{27}$ and $Ni_{473}W_{27}$ at 1830 K. The combined analysis shows the presence of similar short range order in the three samples, with almost no dependence on composition. Icosahedral and bcc-like structures are the most abundant (right figure) but angles are slightly compressed with respect to the perfectly ordered solid (about 60 and 120 degrees).

(a CALculation of PHAse Diagram method) to estimate the Scheil solidification pathway.[17] The solidus and liquidus temperatures were 1582 and 1635 K respectively and these temperatures were used to calculate the approximate liquid compositions at the bottom and top of the solidification zone.[18] The predicted compositions are Ni62.2-Cr11.0-Co5.2-Mo1.3-W1.9-Al10.-Ti5.8-Ta2.3-Nb0.5 and Ni63.0-Cr11.2-Co7.6-Mo0.9-W1.9-Al9.2-Ti4.3-Ta1.6-Nb0.3 at 1635 K and 1582 K respectively. These chemistries include very dilute Nb additions which were removed from the calculations, the balance in composition being spread proportionally over all the remaining species. These compositions then yield the following number of atoms of each species in the 500 atom cell calculations: $Ni_{315}Cr_{56}Co_{38}Mo_5W_{10}Al_{46}Ti_{22}Ta_8$ and $Ni_{312}Cr_{55}Co_{26}Mo_6W_{10}Al_{50}Ti_{29}Ta_{12}$ for 1635 K and 1582 K respectively. These chemistries were then used to construct 500 atom cells with random distributions of the appropriate elements. Simulations are currently underway using an NPT ensemble with Parrinello-Rahman dynamics. These calculations use local density approximation PAW (Projector Augmented Wave) pseudopotentials which were found to give a good representation of the liquid metal superalloy.[14] Improvements in the electron-ion interactions requires a larger cutoff energy for the planewave basis representing the electronic wavefunctions. However, the NPT dynamics allow derivation of the equilibrium volume in a single series of calculations, significantly reducing the required computational effort.

III. RESULTS AND ANALYSIS

The main focus of the AIMD simulations is the calculation of molar volumes for representative binary and ternary alloy compositions in Ni-based superalloys. In calculations of such equilibrium properties for a liquid alloy, it is important to establish that (i) the simulations are run sufficiently long in time to observe appreciable solute inter-diffusion, and (ii) that the periodic system size is large enough to give a realistic liquid structure. If the runs are performed for too short a period, the calculated thermal averages may be biased by the choice of the initial atomic configuration. Further, if the system is too small the positional correlations may not decay sufficiently over the length of the simulation box, giving rise to an artificially enhanced degree of order in the simulated melt structures.

Previously we have reported calculations of liquid alloy diffusion coefficients which address point (i) [15, 16]. From an analysis of mean-square displacements versus time for Ni, Ni-Al, Ni-W and Ni-Re system we demonstrated appreciable diffusion on the time scale of the simulations. For Ni-W measurements of tracer diffusion constants have been recently reported based on experiments which were carefully designed to minimize effects of convection; for a Ni-0.52 at. % W alloy, in the temperature range of 1755-2022 K, the measured tracer diffusion coefficient for W was reported as $2.4(2)\times10^{-5}$ cm^2/s. In our calculations for a $Ni_{473}W_{27}$ alloy at 1830 K, we calculate a value of $2.7(2)\times10^{-5}$ cm^2/s, in excellent agreement with the measured values.

Related to point (ii) we have previously reported structural analyses based on radial distribution functions (RDFs) [15, 16]. These analyses yield partial RDFs for each bond type which reach values near unity at distances significantly less than half the diagonal distance of the simulation cell. The results suggest that the simulation system sizes are large enough to avoid introducing of appreciable order in the liquid structures. The radial-distribution function analyses have also established the presence of pronounced chemical short-range order in the alloy melts. Specifically, the partial distribution functions show clear preferences for the formation of unlike neighbor bonds. Additionally, the bond lengths between unlike neighbors are found to be smaller than expected based on a geometrical average of the like-neighbor nearest-neighbor distances, also implying energetically favorable bonds between unlike species. Further insights into the liquid structure can be obtained from analyses of the topical short-range order, based on a common-neighbor analysis (CNA) [24] and bond-angle distribution functions. Results from such analyses are summarized in

TABLE I: Calculated atomic volumes for molten Ni-alloys at 1750 and 1830 K. The numbers in parentheses represent estimated 95% confidence intervals on the last digit. The calculated (AIMD) results are compared with the predictions of the parameterized model due to Mukai *et al.*.[8] The last column is the ratio of calculated to experimentally measured equilibrium volume at 1830 K. For the Ni-Ta alloys Mukai fit to compositions in the dilute limit (<3.5 at%) making it inappropriate to extrapolate to high solute concentrations.

	V(T=1750 K) (cm^3/mole)		V(T=1830 K) (cm^3/mole)		
Composition	AIMD	Mukai	AIMD	Mukai	$V_{AIMD}/V_{Exp.}$
Al_{500}	12.80(2)		12.91(3)		
Ni_{500}	7.57(1)	7.4597	7.62(1)	7.5727	1.018(1)
$Ni_{400}Al_{100}$	7.88(1)	7.7628	7.94(1)	7.8525	1.011(1)
$Ni_{473}W_{27}$	7.66(1)	7.5534	7.70(1)	7.6557	1.006(1)
$Ni_{400}W_{100}$	7.94(1)	6.5192	7.98(1)	7.3598	
$Ni_{473}Re_{27}$	7.65(1)	7.4940	7.69(1)	7.6557	
$Ni_{400}Re_{100}$	7.91(1)	7.5869	7.93(1)	7.8695	
$Ni_{473}Ta_{27}$	7.70(1)	7.3310	7.75(1)	7.5053	
$Ni_{400}Ta_{100}$	8.14(1)	—	8.18(1)	—	
$Ni_{436}Al_{50}W_{14}$	7.77(1)	7.6920	7.80(1)	7.7682	
$Ni_{436}Al_{50}Re_{14}$		7.6291	7.80(1)	8.2836	
$Ni_{436}Al_{50}Ta_{14}$	7.79(1)	7.6911	7.84(1)	7.8421	

Fig. 1 for pure Ni, $Ni_{473}W_{27}$ and $Ni_{473}Re_{27}$ melts at a temperature of 1830 K. The CNA results in the right panel show a clear preference for the formation of icosahdral short-range order, with a secondary preference for bcc-type order; a much lower distribution of fcc and hcp type clusters are found even though the Ni is a close-packed metal in the solid state. It is worth noting that while a preference for icosahedral and bcc short-range order is clearly demonstrated by the CNA analysis, the liquid clusters are generally not geometrically perfect. This point is also demonstrated by the results of the angular distribution functions on the left panel of Fig. 1. For a perfect icosahedral or bcc cluster one expects bond angles of 120 and approximately 60 degrees; the shift of the peaks in the angular distribution function to slightly lower angles reflects the distortions inherent in the local structural units.

To compute equilibrium values of V, AIMD simulations were performed for a series of volumes at each composition and the average pressure (P) was calculated as the basis for fitting the equation of state. As described previously,[15] for each simulation at a given volume the results show that after an initial short transient, lasting a few tenths of a ps, the pressure displays equilibrium fluctuations about a well defined average value. An analysis of the time scale and amplitude of these equilibrium fluctuations is used to derive estimates of the statistical uncertainties in the calculated time-averaged pressure. For each temperature and composition a total of three to four volumes were considered. The calculated time-averaged pressures were then used to derive an equation of state, assuming a quadratic relationship between P and V. From the fitted equation of state we computed the equilibrium (zero-pressure) volume (V), as well as the bulk modulus and its pressure derivative.[15] Finally, statistical uncertainties were estimated based on the error estimates for each of the individual average pressures. The results are recorded in Table I, listing calculated equilibrium volumes for each of the twelve liquid Ni-based alloy compositions considered to date.

In Table I, values from the most recent parameterization of molten superalloy densities, due to Mukai *et al.*,[8] are listed along side the AIMD results. For elemental Ni, and the binary Ni-Al and Ni-W systems, the Mukai model reproduces well the directly measured densities obtained at these same compositions and temperatures.[6, 7] Thus, for the Ni_{500}, $Ni_{400}Al_{100}$ and $Ni_{473}W_{27}$ systems, a comparison between the Mukai and AIMD results can be considered as representing a direct comparison between experimental measurements and calculations. For elemental Ni the agreement between measured and calculated values of V is at the level of 1.8% at T=1830 K, and 1.5% at T=1750 K. For Ni-Al and Ni-W, the agreement between experiment and theory is comparable, ranging between 0.6% and 1.5% at the two temperatures. For each of these systems the calculated molar volumes are larger than the measurements, a trend that is often found for solid-state *ab-initio* calculations performed within the generalized-gradient approximation to DFT. As a result of the comparisons between experiment and theory for Ni, Ni-Al and Ni-W systems, it is reasonable to conclude that the GGA introduces a positive systematic error in the prediction of the Ni-based liquid atomic volumes, on the order of 0.6–1.8% for the alloy compositions and temperatures considered.

As described in the Introduction, the primary motivation for the present work is to use AIMD simulations as a framework for developing and validating predictive models for $\rho(c,T)$ in Ni-based superalloys. For this purpose, we consider further the most current parameterization for $V(c,T)$ proposed by Mukai *et al.*.[8] We consider cases where there is no experimental data available, and use the AIMD results as a basis for testing the accuracy of the Mukai model in predictions for compositions where it has not been fit. We consider in particular the ternary alloy compositions $Ni_{436}Al_{50}W_{14}$, $Ni_{436}Al_{50}Re_{14}$, and $Ni_{436}Al_{50}Ta_{14}$ listed in Table I. For each of the refractory elements (X=W, Re or Ta), these compositions represent an average of those for the binary $Ni_{400}Al_{100}$ and $Ni_{473}X_{27}$ melts also considered in this work. The AIMD results predict that the volumes of the ternary melts are all very well approximated (to within 0.2%) by a linear interpolation between the binary alloy values. By contrast, the Mukai model predicts significant deviations (as much as 7%) from linearity for the ternary alloys containing Re and Ta. These results highlight the

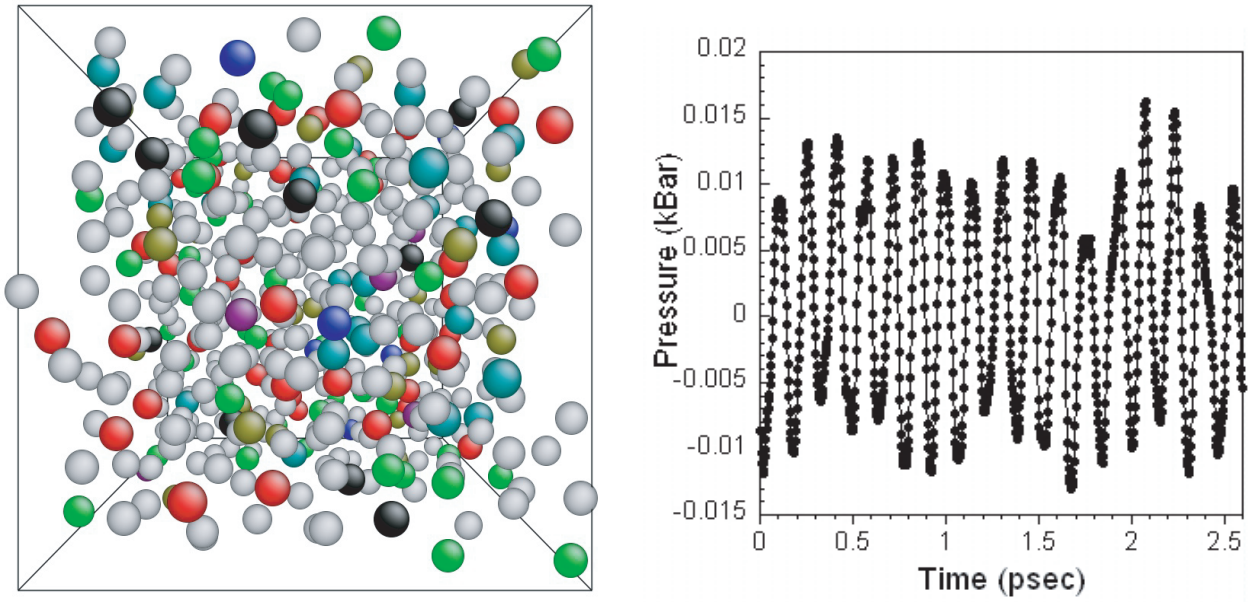

FIG. 2: Schematic of the 500 atom cell (left) and the evolution of the internal pressure (right) over a 2.6 psec interval for an NPT simulation of an eight component RENE-N4 alloy. The colors of the atoms correspond to the following elements Ni-light grey, Cr-green, Co-gold, Mo-purple, W-blue, Al-red, Ti-cyan, Ta-black.

limited accuracy of the Mukai parametrization for alloy compositions outside the range where experimental data was available for the model fitting. The current AIMD results provide additional data which will be useful to refine the desity parameterization and extend its range of applicability.

The constant pressure (NPT) AIMD method was initially tested by calculating the equilibrium volume of $Ni_{400}Re_{100}$ at 1750 and 1833 K, allowing direct comparison of the NVT and NPT statistics. After approximately 5 psec the NPT calculations produce equilibrium volumes of 7.89(1) and 7.94(1) (cm^3/mole) for 1750 and 1833 K respectively that are within 0.26% of the NVT calculations. Another set of NPT calculations on model RENE-N4 alloys are currently underway. A plot of the instantaneous pressure over the first 2.6 psec of a representative simulation is shown in Fig. 2 illustrating the stability of the NPT-AIMD method. Pressure oscillations have an amplitude of approximately 15 kBar with a period of 160 fsec. Even for these complex chemistries the NPT method allows for relatively long, 3fs, time steps. Refinement of the input parameters, controlling the time integration of the NPT ensemble, is expected to improve the performance of this technique. We are currently running several instantiations of the RENE-N4 alloys, based on different random arrangements of the atomic species, at the target temperatures as discussed in the Methods section.

IV. SUMMARY

AIMD simulations have been performed to derive liquid-phase atomic volumes for twelve elemental, binary and ternary alloy compositions of molten Ni with Al, W, Ta, and Re additions to compute atomic volumes at temperatures of 1830 and 1750 K. Comparisons between AIMD results and direct measurements for Ni, Ni-Al, Ni-Ta, and Ni-W yield agreement at the level of 0.6–1.8%, with the calculated volumes being systematically larger than experimental volumes. Simulations were performed for ternary alloy compositions containing W, Re and Ta, from which accuracy limits were assessed for the most recently published density parameterization at alloy compositions outside the range where experimental data is presently available. Overall our results demonstrate the high accuracy attainable with AIMD, and the utility of this method for providing data where experimental is unavailable, as the basis for refining the development of density models for superalloy solidification.

Future work will involve further AIMD calculations to more thoroughly test, and refine as necessary, the accuracy of the current published parameterization for $V(c,T)$ over range of compositions and T relevant for superalloy solidification. The recently developed NPT implementation of VASP will be used to further refine the thermal expansion of the binary and ternary alloys. This method will also be used to study short range ordering, multi-component diffusion and $V(c,T)$ for an eight-component model RENE-N4 superalloy which is the current focus of an experimental effort aimed at validation of Rayleigh-number criterial for the prediction of the formation of freckles and related solidification defects. Finally we will run alloy compositions for several other Ni-based superalloys and compare predictions to the limited experimental measurments of liquid metal densities.

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[1] J. R. Sarazin and A. Hellawell, Met. Trans. **19A**, 1861 (1988).
[2] T. M. Pollock and W. H. Murphy, Met. Trans. A **27A**, 1081 (1996).
[3] P. Auburtin, S. L. Cockcroft, and A. Mitchell, *Superalloys 1996* (TMS, Warrendale, PA, 1996), pp. 443.
[4] C. Beckermann, J. P. Gu and W. J. Boettinger, Met. Trans. A **31A**, 2545 (2000).
[5] J. E. Spowart and P. W. Voorhees, work in progress.
[6] K. Mukai, L. Fang, Z. Li and F. Xiao, Mater. Trans. **45**, 1754 (2004).
[7] K. Mukai, Z. S. Li and F. Liang, Mater. Trans. **45**, 2987 (2004).
[8] K. Mukai, Z. S. Li and K. C. Mills, Met. Mater. Trans. B, **36**, 255 (2005).
[9] S. Nosé, J. Chem. Phys. **81**, 511 (1984); Mol. Phys. **52**, 255 (1984).
[10] W. G. Hoover, Phys. Rev. A **31**, 1695 (1985); **34**, 2499 (1986).
[11] G. Kresse and J. Hafner, Phys. Rev. B **47**, 558 (1993).
[12] G. Kresse and J. Hafner, Phys. Rev. B **49**, 14251 (1994).
[13] G. Kresse and J. Furthmüller, J. Computat. Mater. Sci. **6**, 15 (1996).
[14] G. Kresse and J. Joubert, Phys. Rev. B **59**, 1758 (1999).
[15] M. Asta, D. R. Trinkle and C. Woodward, Proceedings 2006 HPC-UGC, (IEEE Computing Society, Los Alamitos, CA, 2006), pg. 177-181.
[16] M. Asta, D. R. Trinkle and C. Woodward, Proceedings 2007 HPC-UGC, (IEEE Computing Society, Los Alamitos, CA, 2007), pg. 147-152.
[17] See for example: S.-.L. Chen, F. Zhang, S. Daniel, F.-Y. Xie, X.-Y. Yan, Y.A. Chang, R. Schmid- Fetzer, and W.A. Oates, Journal of Metals, Vol. 55, Num. 12, 48 (2003).
[18] Private communication, J. Madison and T. Pollock, Department of Materials Science and Engineering, University of Michigan, 2008.
[19] M. Asta, D. Morgan, J. J. Hoyt, B. Sadigh, J. D. Althoff, D. de Fontaine, and S. M. Foiles, Phys. Rev. B **59**, 14271 (1999).
[20] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).
[21] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996).
[22] J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13244 (1992).
[23] J. P. Leonard, T. J. Renk, M. O. Thompson and M. J. Aziz, Met. Mater. Trans. A **35A**, 2803 (2004).
[24] J. D. Honeycutt and H. C. Andersen, J. Phys. Chem. **91**, 4950 (1987).
[25] J. Lill, D. R. Trinkle and C. Woodward, unpublished work (2007).